DIMERIZATION IN POLAR GASES

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ABSTRACT The semi-empirical method of Hirschfelder, McClure and Weeks and the statistical approach of calculating the percentage of dimers formed in a polar gas have been compared for several substances. The results indicate the limitation of Hirschfelder et al's approach and also point to the necessity of considering the presence of metastable dimers for the calculation of the equilibrium constant for dimerization.

INTRODUCTION

The consideration of cluster formation is necessary for representing properly the properties of dense gases (Das Gupta and Barua, 1965). As a first step in this direction it is necessary to consider dimerisation only which is sufficient upto a certain density limit. The dimers consist of bound and metastably bound double molecules. Recently the idea of quasi-dimers has also been introduced (Kim and Ross, 1965). In the present paper we shall confine our consideration to bound double molecules only. The dimers thus formed may be defined as systems whose relative kinetic energy is less than the negative value of the mutual potential energy (Hirschfelder, McClure and Weeks, 1942). The number of dimers is determined by the usual chemical equilibrium constant although the lifetime of these molecules is of the order of the collision time.

The formation of dimers in non-polar gases has been considered by Stogryn and Hirschfelder (1959) for realistic intermolecular potentials. However, for polar gases due to the presence of long-range dipole-dipole forces association plays a much more important part than in non-polar gases. Hirschfelder, McClure and Weeks (1942) suggested a semi-empirical method for calculating the mole fractions of dimers in a polar gas. According to this method, the equilibrium constant for dimerisation is given by,

$$K(T) = b_a - B(T) = n_2 V / n_1^2 \qquad \ldots (1)$$

where n_1, n_2 are the moles of monomers and dimers respectively and V is the volume. b_a is a constant depending on the intermolecular forces and $B(T)$ is the second virial coefficient at temperature T.

However, another approach which is more logical and accurate is from the stand point of statistical mechanics. The second virial coefficient $B(T)$ can be written as follows

$$B(T) = B_f(T) + B_b(T) + B_m(T) \qquad \ldots (2)$$

where $B_f(T)$, $B_b(T)$ and $B_m(T)$ are the contributions of the free, bound and metastably bound double molecules. When metastably bound molecules are neglected the equilibrium constant for dimerisation may be written as,

$$K(T) = b_0 B_b^*(T^*) \qquad \ldots (3)$$

where $$b_0 = \frac{2\pi}{3} N\sigma^3$$

Recently Barua, Chakraborti and Saran (1965) have calculated $B_b^*(T^*)$ for a polar gas by assuming the dipoles to act in the head-to-tail position according to the Stockmayer potential,

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] - \frac{\mu^2}{r^3}\ (2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi), \qquad \ldots (4)$$

where μ is the dipole moment of the interacting molecules, θ_1 θ_2 are the angles of inclination of the axes of the two dipoles to the line joining the centre of the molecules and ϕ is the azimuthal angle between them, σ and ϵ have usual significance.

When the dipoles are in the head-to-tail position Eq. (4) becomes

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad \frac{2\mu^2}{r^3} \qquad (5)$$

The final expression for $B^*{}_6(T^*)$ calculated on the basis of Eq (5) is given by (Barua *et al*, 1965)

$$B_b^*(T^*) = -\frac{16}{(\pi)^{\frac{1}{2}}} \sum_{n=0}^{\infty} \frac{4^n(n+1)!}{(2n+1)!} \times \frac{1}{2n+1} \left[\frac{4(A\ Y_n^2 - Y_n^6)}{T^*}\right]^n \qquad . (6)$$

where $A = \mu^{*2}/2$, $\mu^* = \mu/\sqrt{\epsilon\sigma^3}$ (μ being the dipole moment) $Y = (r/\sigma)^{-3/2}$ and $T^* = kT/\epsilon$ The values of $B_b^*(T^*)$ corresponding to different values of A and T^* have been tabulated It has, however, recently been pointed out by Barua, *et. al* (1966) that it is physically much more realistic to assume an 'effective' relative orientation of the dipoles of the interacting molecules. This means that at any particular temperature and pressure although the different pairs of colliding molecules interact with a different relative orientation, it is possible to assume an 'effective' relative orientation with which all the pairs interact on the

$$A = \frac{\mu^{*2} g_{eff}}{4} \quad ; \quad g = (2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi), \qquad (7)$$

average. Under this condition. It is possible to utilise the Table $B_b^*(T^*)$ as obtained by Barua *et al* (1965) for 'effective' relative orientation of dipoles as given by A from Eq. (7).

In view of the importance of the problem we thought it necessary to compare the different methods which are at present available for the calculation of the mole-fractions of dimers.

CALCULATION AND RESULTS

For the purpose of comparison, we have chosen ammonia, chloroform and methyl chloride for which both second virial and viscosity data are available. The force constants σ, ϵ/k and A used for the calculation of $B_b^*(T^*)$ are shown in Table I For ammonia and methylchloride it is not possible to fit the experimental viscosity data for $g = 2$ (Itean, Glueck and Svehla, 1961 and Barua *et al*, 1966) Consequently we have used only g_{eff} values obtained by fitting viscosity data by using collision integrals calculated by Monchick and Mason. (1961). For the for method suggested by Hirschfelder *et al* (1942) except for ammonia the value of b_a was obtained from the relation

$$b_a = 1.75 V_c$$

V_a being the critical volume For ammonia b was obtained by fitting to experimental data (Hirschfelder, *et al*, 1942). Results of the sample calculations performed are shown in Table II.

DISCUSSION OF RESULTS

It may be seen from Table II that for chloroform and methyl chloride the mole fractions of dimers obtained by using the semi-empirical method of Hirschfelder *et al*, is much higher tha those obtained by using Eq. (3). For ammonia the agreement between the two methods is fairly good. This is most probably due to the reason that for ammonia the constant b_a was obtained from experimental data which indirectly shows that b_a as given by Eq. (8) gives too high value of the mole-fraction of dimers Another source of discrepancy between the two methods of calculation is the neglect of metastably bound double-molecules in calculating $K(T)$ from Eq. (3) Therefore, it appears that $K(T)$ as obtained from Eq (3) give reliable values of the molefractions of dimers provided metastable double double molecules are also considered.

TABLE I

Force parameters used for the calculation of $B_b^*(T^*)$

Substance	σÅ	ϵ/k°K	A	Reference
Chloroform	5 513	256.7	0.086	a
Methyl Chloride	4.870	72 4	0 60	Present work
Ammonia	2.733	380	0.25	b

a. Itean. E. C., Glueck, A. R., and Svehla, R. A., 1961, Nasa Technical Note D—481.

b. Barua, A. K, Saran, A., and Singh, Y, 1966, To be published.

TABLE II

Molefractions of dimers at different pressures and temperatures

Substance	T°K	P atms	x_2	
			From Eq (1)	From Eq (3)
		1	0 0598	0 0189
		5	0 2108	0 0826
	298	10	0 3162	0 1439
		25	0 4721	0 2651
		50	0 6293	0 3788
		1	0 0396	0 0121
		1	0.1537	0 0551
Chloroform	348	10	0 2447	0 1004
		25	0 3940	0 1900
		50	0 5116	0 3021
		1	0 0282	0 0084
		5	0 1168	0 0392
	398	10	0 1940	0 0730
		25	0 3314	0 1525
		50	0 4506	0 2432
		1	0 0387	0 0121
		5	0 1509	0 0554
	255	10	0 2411	0 1004
		25	0 3897	0 1991
		50	0 5076	0 3043
		1	0 0194	0 0055
		5	0 0845	0 0265
Mothyl Chloride	338	10	0 1467	0 0504
		25	0 2691	0 1105
		50	0 3832	0 1853
		1	0 0105	0 0029
		5	0 0844	0 0143
	450	10	0.0886	0 0279
		25	0.1795	0.0645
		50	0 2780	0 1164
		1	0 0185	0 0154
		5	0 0992	0 0688
	273	10	0 1414	0 1224
		25	0 2616	0 2334
		50	0 3749	0 3428
		1	0 0094	0 0079
		5	0 0435	0.0374
	333	10	0 0804	0.0698
		25	0 1654	0 1467
		50	0 2601	0 2357
Ammonia				
		1	0 0048	0 0039
		5	0 0228	0 0188
	423	10	0 0437	0 0364
		25	0 0973	0 0825
		50	0 1622	0 1438
		1	0 0028	0 0021
		5	0 0138	0.0101
	523	10	0 0281	0 0198
		25	0.0621	0.0468
		50	0 1119	0.0860

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REFERENCES

Barua, A. K., Chakraborti, P. K , and Saran, A , 1965, *Mol. Phys* , 9
Barua, A K , Saran, A , and Singh, Y , 1966, to be published
Das Gupta, A , and Barua, A K , 1965, *J Chem. Phys* , **42**, 2849
Hirschfelder, J O , McClure, F T., and Weeks, I F , 1942, *J Chem. Phys* , **10**, 201
Itean, E C , Glueck, A R , and Svehla, R A , 1961, *NASA Technical Note* D-481
Mason, E. A , and Monchick, L , 1961, *J. Chem Phys* , **35**, 1676
Monchick, L,, and Mason, E A , 1965, *J. Chem. Phys.*, **42**, 263
Stogryn, D. E., and Hirschfelder, J. O., 1959, *J. Chem. Phys.*, **31**, 1531.